Oak Ridge National Laboratory

Project ID: bat397

June 03, 2020

Titanium Niobium Oxide-Based Lithium-Ion Batteries for Extreme Fast-Charging Applications

<u>Sheng Dai</u>,

Xiao-Guang Sun, Jianlin Li, Hailong Lyu

2020 DOE Vehicle Technologies Office Annual Merit Review

The University of Tennessee Knoxville

BIG ORANGE. BIG IDEAS.®

Overview

Timeline

- Task Start: 7/1/18
- Task End: 6/30/20
- Percent Complete: 70%

Budget

- Total task funding
  - $720k
- $360k in FY19
- $360k in FY20

Barriers

- Barriers Addressed
  - Existing chemistries needs improvement in XFC and energy density.
  - Abuse Tolerance.
  - Achieve deep discharge cycling of 1000 cycles for EVs by 2022.

Partners

- Collaboration: ORNL
- Project Lead: University of Tennessee

Relevance & Objectives

- Relevance: Graphite is susceptible to Li plating due to the proximity of the LiC_x potential to that of Li/Li^+, which limits the charging current density and also results in capacity fade and safety concern.

- Main Objective: Develop TNO based anode materials with high electronic conductivity and high capacity for extremely fast charging applications with 180 Wh/kg.
- Objectives in this period

➤ Enhance the electronic conductivity and lithium diffusion coefficient of TNO by transition metal doping.

➤ Improve the long cycling stability of TNO based full cells by new lithium malonatoborate salts additives.

Gallagher, K. G., et al., *J. Electrochem. Soc.* **2015,** *163* (2), A138-A149.

Project Milestones

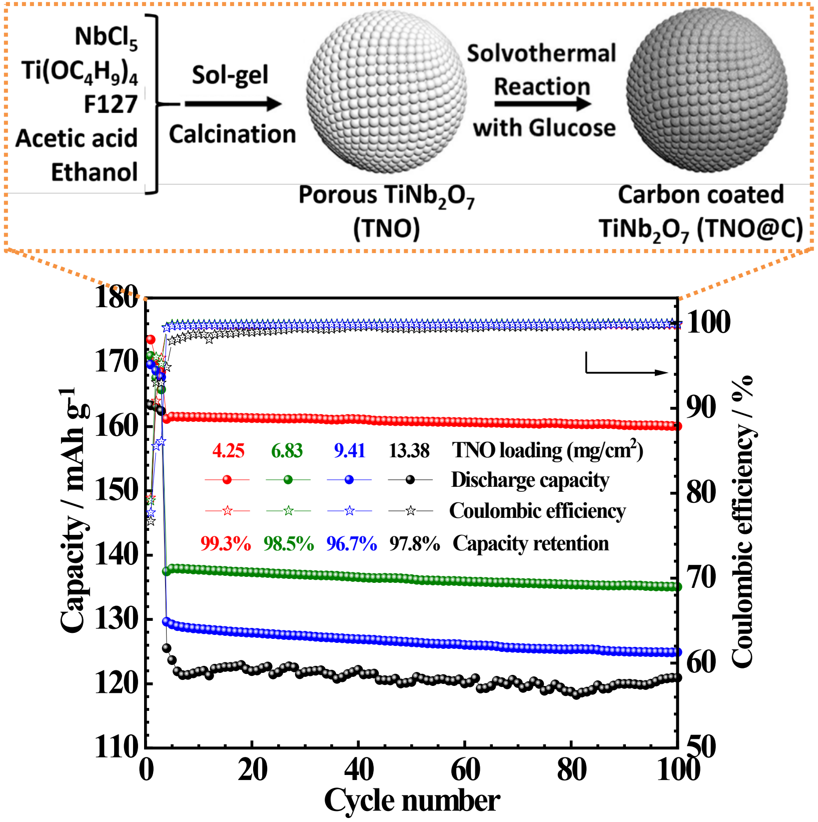
Date	Milestones and Go/No-Go Decisions	Status
Oct. 31, 2019	Milestone 5 Finish evaluation of transition metal doped TNO.	Ongoing
Dec. 31, 2019	Milestone 6 Finish evaluation of new lithium malonatoborate salts as additives in half cells.	Ongoing
Mar. 30, 2020	Go/No-Go Decisions Determine whether the new additives have better performance than commercially available additives.	Ongoing
April 30, 2020	Milestone 7 Finish optimization of transition metal doped TNO based full cells using coin cells.	On track
July 31, 2020	Milestone 8 Finish fabrication of 18 2Ah pouch cells and deliver them to DOE.	On track

Project Approach

- **Problems:**
  - Electronic conductivity of TNO is low
  - Achieved capacity is much lower than theoretical capacity
  - The energy density of the cells is low with extremely fast charging
- **Technical approach and strategy:**
  - Enhance rate capability by formation of porous structure
  - Improve electronic conductivity by doping with metal ions and surface coating with carbon
  - Synthesize large scale TNO with low cost alternative precursors
  - Evaluate rate performance and long term cyclability of coin cells using high loading TNO
  - Improve long term cyclability of full cells by pairing TNO with high energy and high voltage NMC622 cathode using functional additives
  - Evaluate energy density and extremely fast charging performance of TNO and NMC622 based pouch cells

Guo, Hu, Goodenough, Dai et al, *Energy Environ. Sci.*, 2014, 7, 2220.

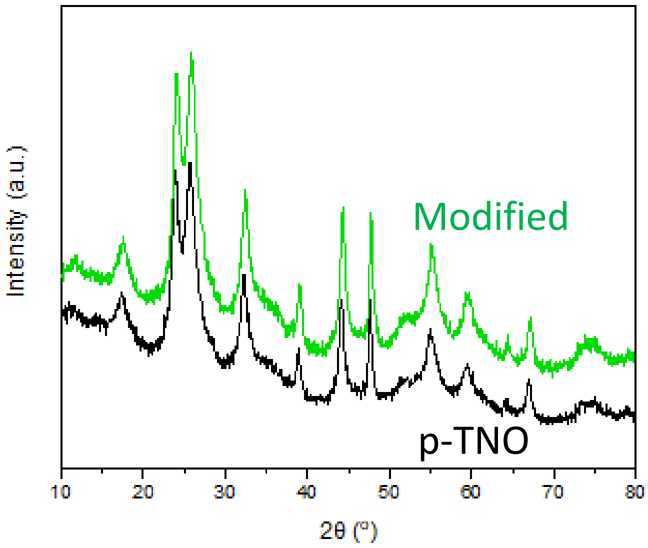
Accomplishments: Summary of FY 19

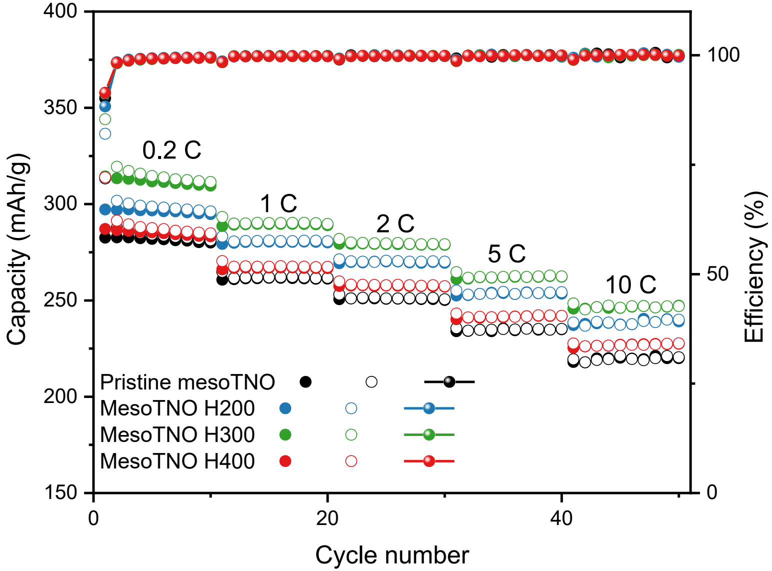


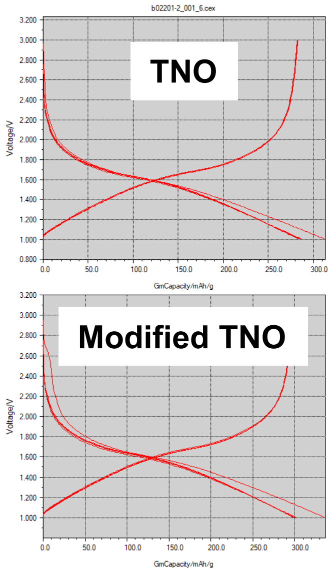
- Carbon coated porous $TiNb_2O_7$ material (**TNO@C**) was synthesized with low-cost niobium chloride and glucose by facile sol-gel and hydrothermal methods.

- The loading of the active material is crucial to the performance of NMC622/TNO@C full-cells under 10 min fast charge protocol.

Modified TNO exhibits higher specific capacities

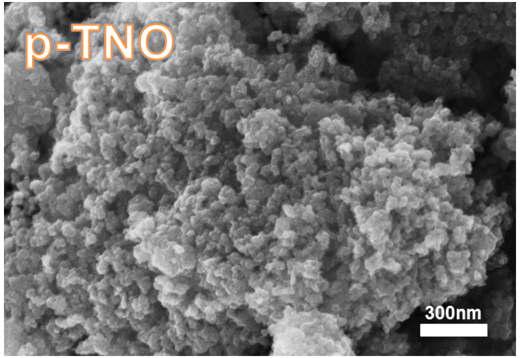


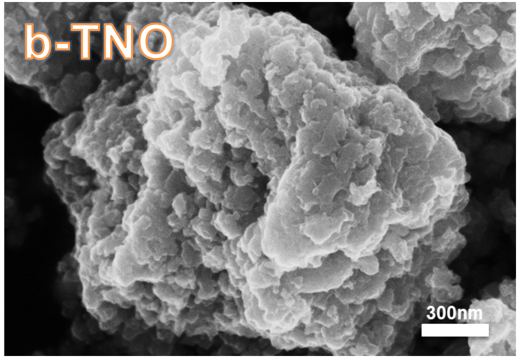


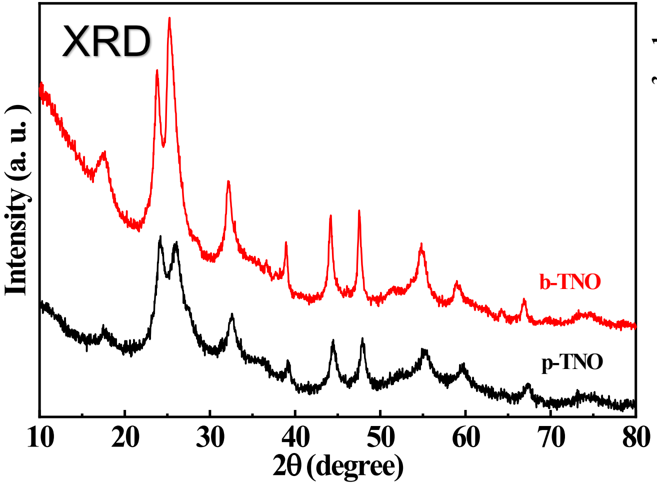


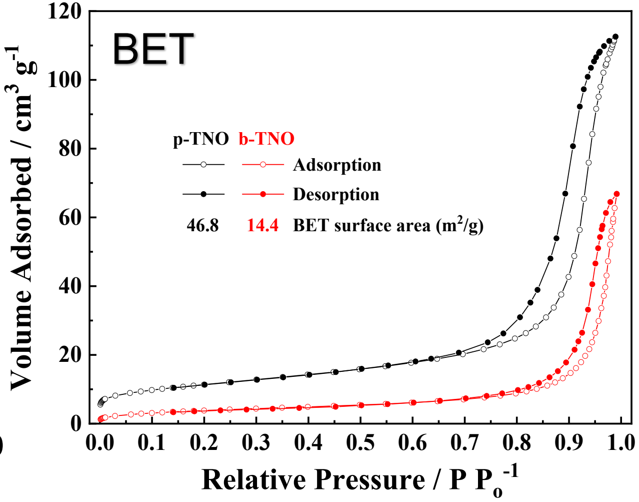
- ➢ Modified TNO can maintain the XRD structure of TNO, meanwhile, increase the capacities of TNO under different rates.
- ➢ A modified TNO under 300 °C delivers specific capacities about 40 mAh/g higher than that of the pristine TNO under each rate.

Accomplishments: Synthesis of bulk TNO



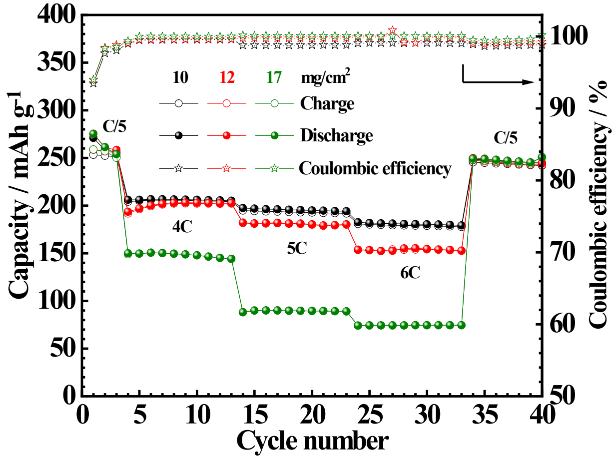


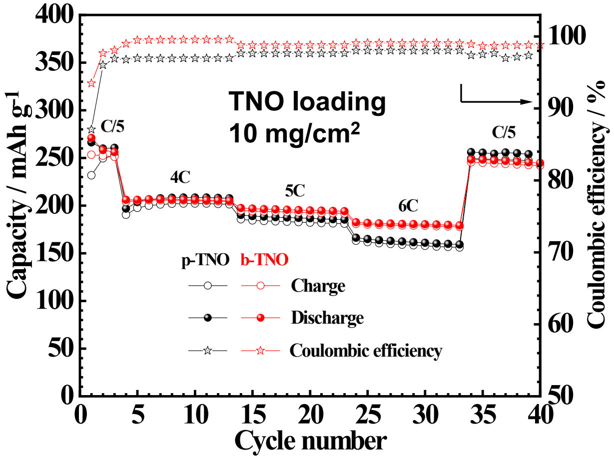


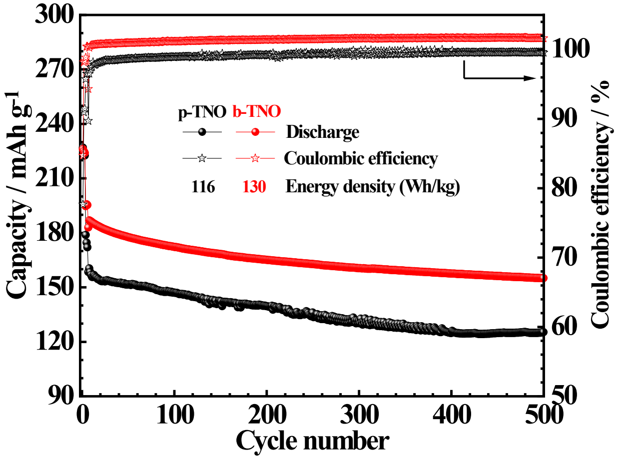


- Bulk TNO (b-TNO) was synthesized without templating agents, exhibiting lower surface area.
- The structure of b-TNO is similar to that of p-TNO but with larger primary particles, consistent with its better crystallinity from the XRD results.

Accomplishments: Evaluation of b-TNO anode





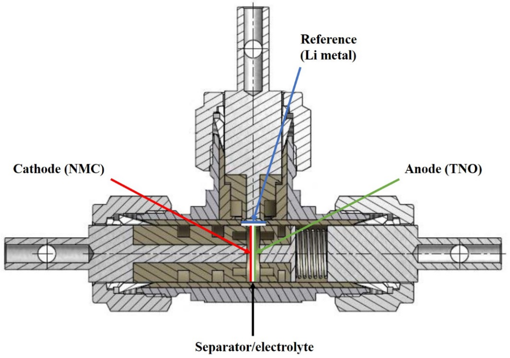


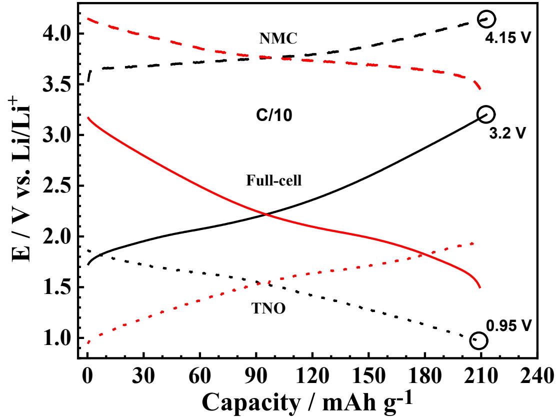
- Due to less interfacial reactions, the initial coulombic efficiency of the b-TNO half-cell (93.5%) is higher than that of the p-TNO half-cell (87.1%).
- Active material loading is still a major factor for high rate performance of b-TNO half-cells.
- Both b-TNO based half-cell and full-cell show better performance than those of p-TNO based cells.

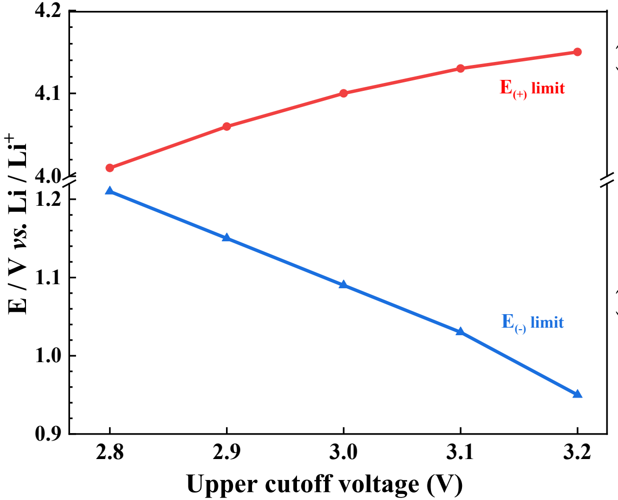
$$U=E/(m_c+m_a)\times10^6\times0.85$$

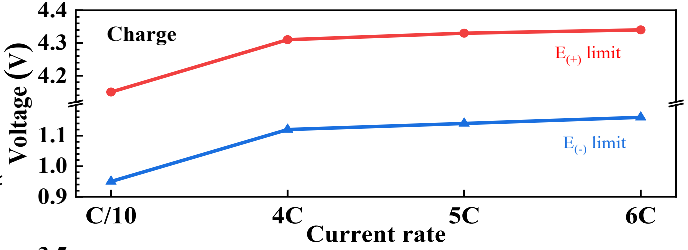
- *U* – Energy density (Wh/kg)
- *E* – Energy (Wh)
- m_c – Cathode mass (mg)
- m_a – Anode mass (mg)
- *0.85* – Assuming the electrodes occupy 85% of the pouch cell weight

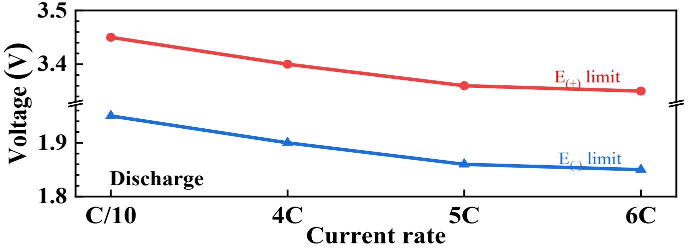
Accomplishments: 3-Electrode Cell Investigation







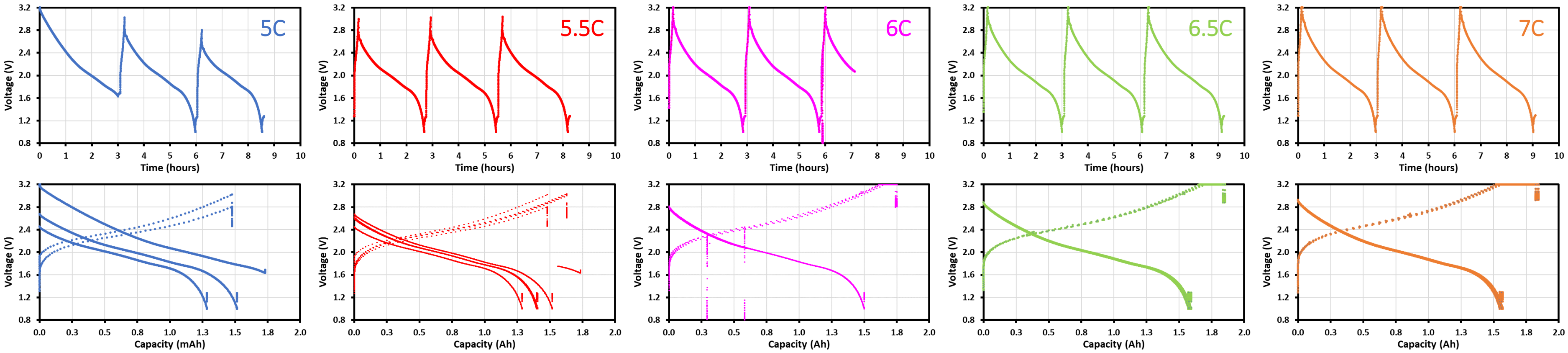




- $E_{(+)}$ increases with increase of both upper cutoff voltage and charge rate.
- Higher rates cause more polarization of the NMC cathode than the TNO anode.
- 3.2 V is selected as the upper cutoff voltage to keep $E_{(+)}$ within the stability window of the NMC cathode.

Lyu, Li, Sun, and Dai et al, *ACS Applied Energy Materials,* 2020, under revision.

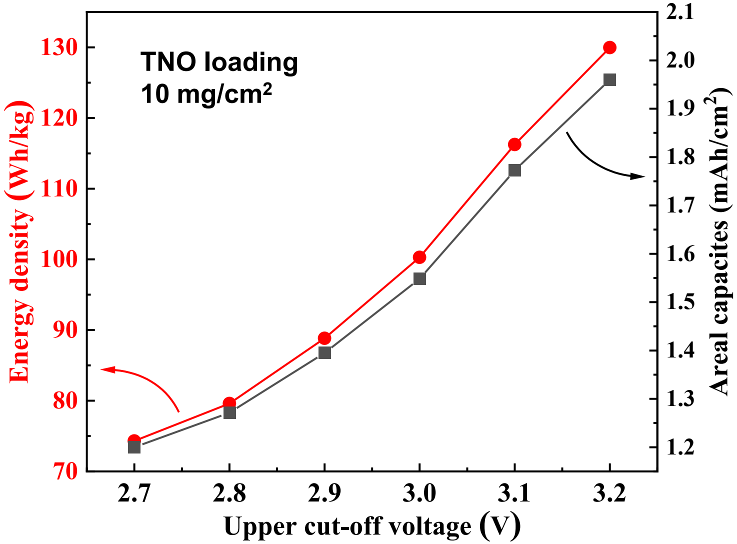
Accomplishments: Optimization of pouch cells

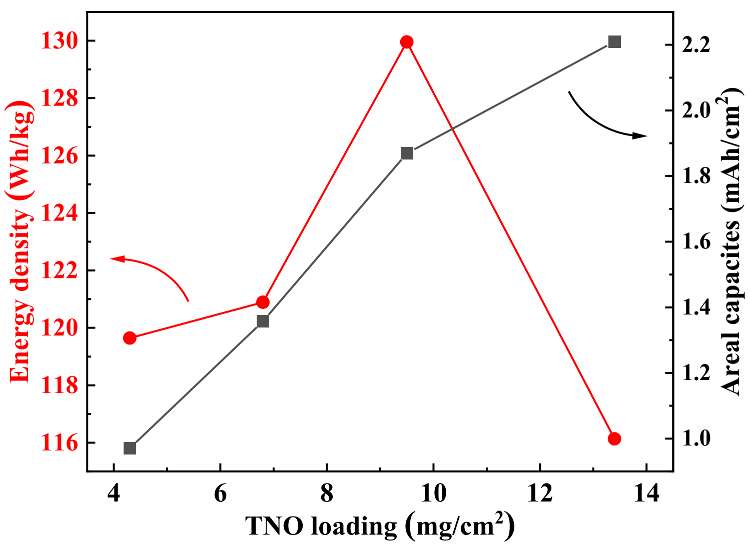


Charge capacity (Ah)	5C	5.5C	6C	6.5C	7C
Constant current (CC)	1.5	1.62	1.63	1.66	1.52
Constant voltage (CV)	N/A	N/A	0.12	0.18	0.3
Total	1.5	1.62	1.75	1.84	1.82

- A charging rate of 6.5C is the best choice for the NMC/TNO pouch cells to achieve higher capacities under XFC condition.

Accomplishments: Optimization of energy density





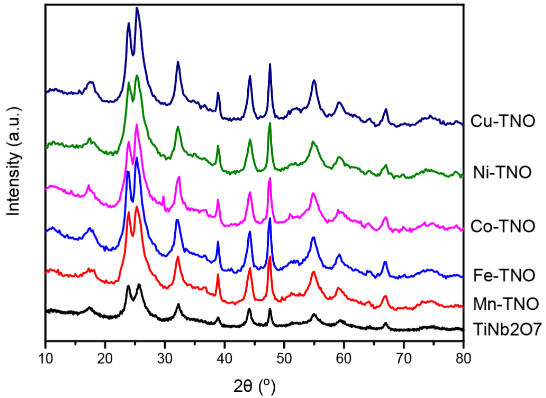
➢ The full-cell with a TNO loading of 9.5 mg/cm^2 exhibits the highest initial discharge energy density of 130.0 Wh/kg.

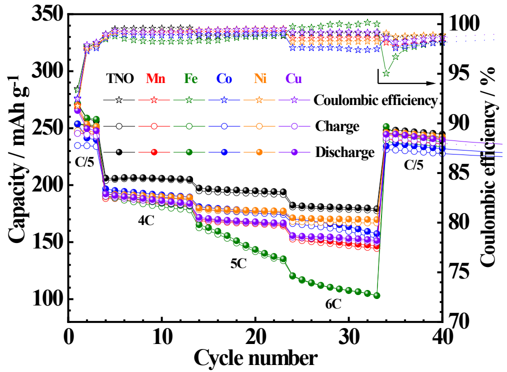
➢ Energy densities and areal capacities of the full-cells increase with increasing the upper cut-off voltage.

TNO loading (mg/cm^2)	4.3	6.8	9.5	13.4
Mass energy density (Wh/kg)	119.6	120.9	130.0	116.1
Volume energy density (Wh/L)	299	302	325	290
Energy retention after 500 cycles (%)	96.5	92.7	85.6	88.5

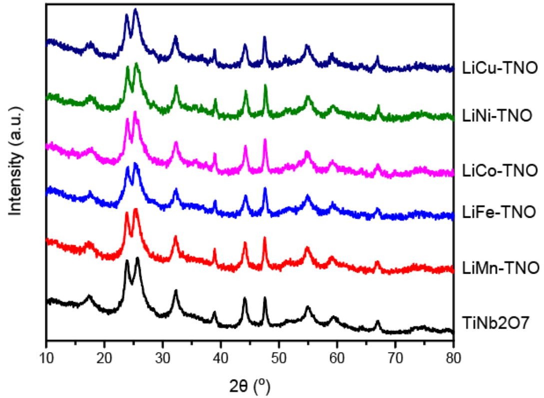
Lyu, Li, Sun, and Dai et al, *ACS Applied Energy Materials,* 2020, under revision.

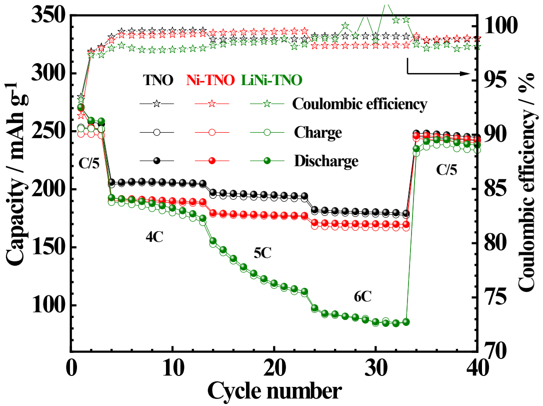
Accomplishments: Transition metal doped TNO





- The crystal structure of TNO is barely affected by the 2% transition metal doping.
- The Mn, Fe, Co, Ni, or Cu doped TNO can not deliver better high rate performance than pristine TNO.

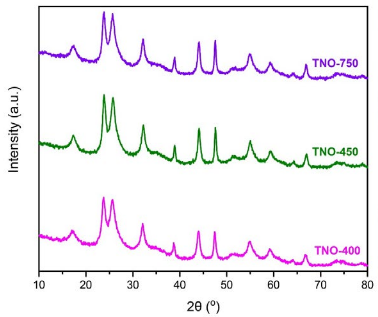


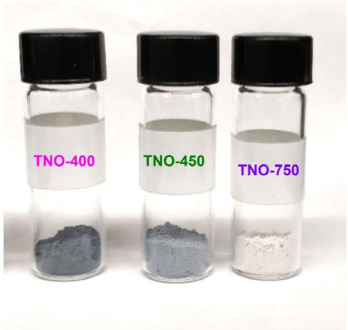


- The crystal structure of TNO is well maintained after lithium/ transition metal co-doping ($Li_{0.04}M_{0.02}Ti_{0.98}Nb_2O_7$).
- The lithium/nickel co-doped TNO cannot deliver better high rate performance than Ni-doped and pristine TNO.

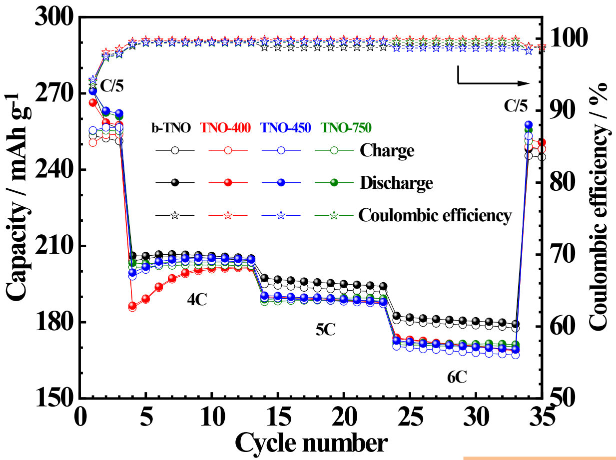
Grey et al, *J. Am. Chem. Soc.*, 2019, 141, 16706-16725.

Accomplishments: Investigation of carbon doping



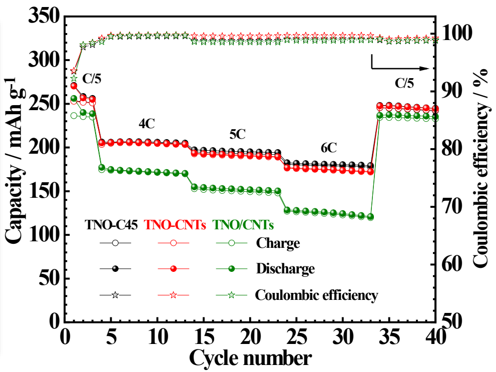


TNO precursor with F127
- 400 °C Air 2h + 750 °C N_2 2h → TNO-400 0.5 wt% C 45 m²/g
- 450 °C Air 2h + 750 °C N_2 2h → TNO-450 0.2 wt% C 40 m²/g
- 750 °C Air 2h → TNO-750 0 wt% C 30 m²/g



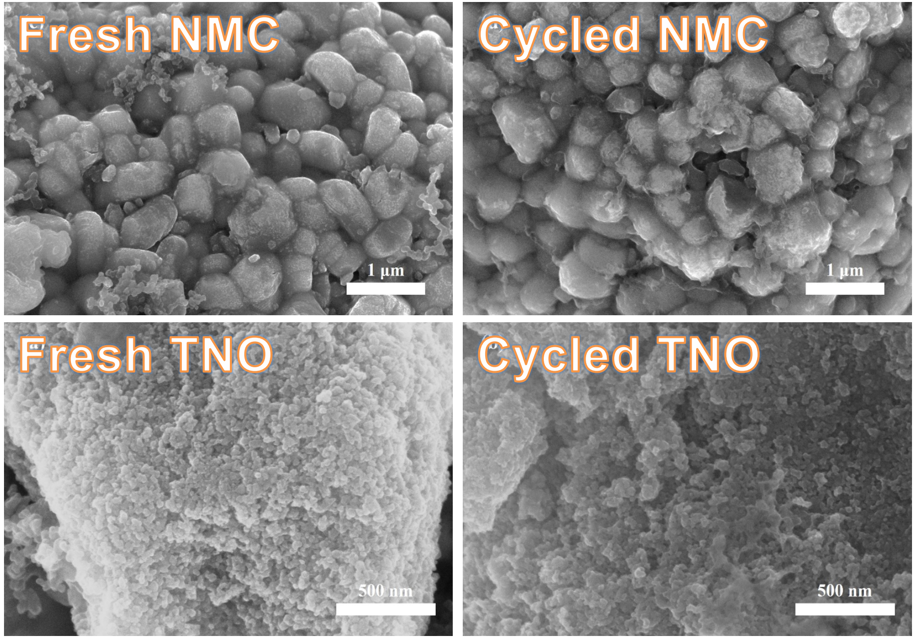
- The in-situ carbon doping strategy is less efficient than previously reported carbon coating approach using glucose.

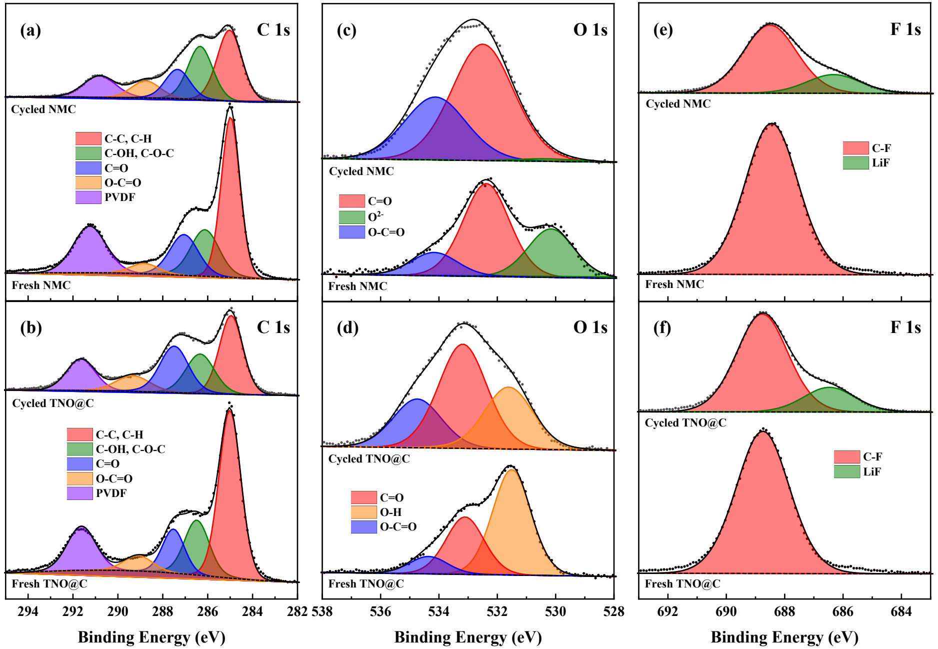
- CNTs doped TNOs using either in-situ doping (TNO/CNTs) or electrode cast (TNO-CNTs) can not achieve better high rate performance than that casted with TNO-C45.



	Active materials	C45	CNTs	PVDF
TNO-C45	80% b-TNO	14%	0%	6%
TNO-CNTs	80% b-TNO	7%	7%	6%
TNO/CNTs	90% TNO/CNTs (10% CNTs)	4%	0%	6%

Accomplishments: Cycled NMC and TNO electrodes





- Lithium plating are suppressed by the high-voltage anode material TNO under XFC conditions, but the surface –OH group might be responsible for gassing of the pouch cells during cycling.
- SEI and passivation layers on the cycled NMC and TNO electrodes are evidenced by the reduced signal of PVdF binder in C 1s, increased carbonyl signal in O 1s, and the presence of LiF signal in F 1s.

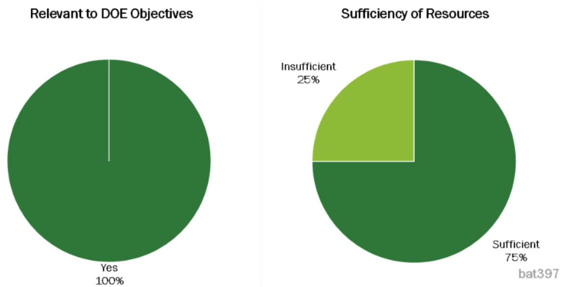
OAK RIDGE National Laboratory

Lyu, Li, Sun, and Dai et al, *ACS Applied Energy Materials,* 2020, under revision.

BIG ORANGE BIG IDEAS

Response to Previous Year Reviewers' Comments

- "Specific energy of the full cell, as well as areal capacity, needs to be reported."
  - The related information has been provided in slide 11.
- "The limited specific energy density due to narrow working voltage range for the battery with TNO may limit its application."
  - While we agree with the reviewer's opinion, we would emphasize that the beauty of using of TNO as anode in fast charge batteries in electric vehicles can tolerate abuses without worrying the safety related issue in graphite based full cells. This can simplify pack design which could reduce the pack weight and volume and compensate the relatively low energy density from cell level. Also, in this project, we are trying to improve the specific energy density of TNO based full cells by increasing the specific capacity of TNO and pairing with suitable cathodes with higher capacities and voltages.
- "Timeline seems aggressive for the remaining work."
  - We have applied for a one-year extension for our project.
- "More funding would be needed to develop large format cells."
  - We are seeking other opportunities to co-develop and validate the technology in large format cells



Collaboration and Coordination

Partners

- National Labs: Oak Ridge National Laboratory
  - Development of electrolyte and battery evaluation
  - Large format pouch cell fabrication and evaluation
- Active Material Suppliers: TODA America, ConocoPhillips
  - Providing NMC622 powders and conductive carbon
- Inactive Material Suppliers: Solvay Specialty Polymers
  - Providing binder polymer

Remaining Challenges and Barriers

- Unlike other projects, this project needs to synthesize all the anode materials for large format pouch cells, which requires great efforts and time.
- The accomplished energy density is still far below the target required by DOE since the average full cell voltage is reduced by the high voltage TNO anode.
- During the preliminary evaluation of NMC/TNO pouch cells, we have found a gassing issue that significantly affects the long cycle stability of the full cells.

Proposed Future Research

- Continue to improve the specific capacity of TNO under high rates.
  - Anion doping to replace oxygen ions
  - Low-valence titanium cations self-doping *via* structural modification
  - Partially replace niobium with other cations
- Improve the energy density of full cells by increasing the cell voltage.
  - Increase the upper cut-off voltage of the full cells
  - Decrease the potential of TNO *via* elemental doping
- Investigate the gassing issue of NMC/TNO pouch cells.
  - Investigate the gassing mechanism of TNO pouch cells
  - Suppress the gassing issue of the TNO anodes by surface coating and high temperature treatment

Summary

- Bulk TNO (b-TNO) was successfully synthesized without using templating agent.
- The b-TNO exhibits enhanced properties than p-TNO.
- An upper cut-off voltage of 3.2 V was confirmed for NMC/TNO full cells *via* a three-electrode Swagelok cell experiment.
- Large format 2Ah pouch cells were fabricated, evaluated, and delivered to DOE.
- The effects of upper cut-off voltages and TNO loadings on the energy densities and areal capacities of the full-cells were investigated and optimized.
- Different doping strategies, such as transition metal doping, lithium doping, transition metal and lithium co-doping, carbon doping, were investigated to improve the high rate performance of the TNO anodes.
- A modification strategy was developed to further enhance capacities of TNO.
- The NMC and TNO electrodes after 500 XFC cycles were investigated, proving the existence of surface passivation layers.

Acknowledgements

- U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (Program Managers: Adrienne L. Riggi, Brian Cunningham, David Howell)

ORNL Contributors: Xiao-Guang Sun, Jianlin Li

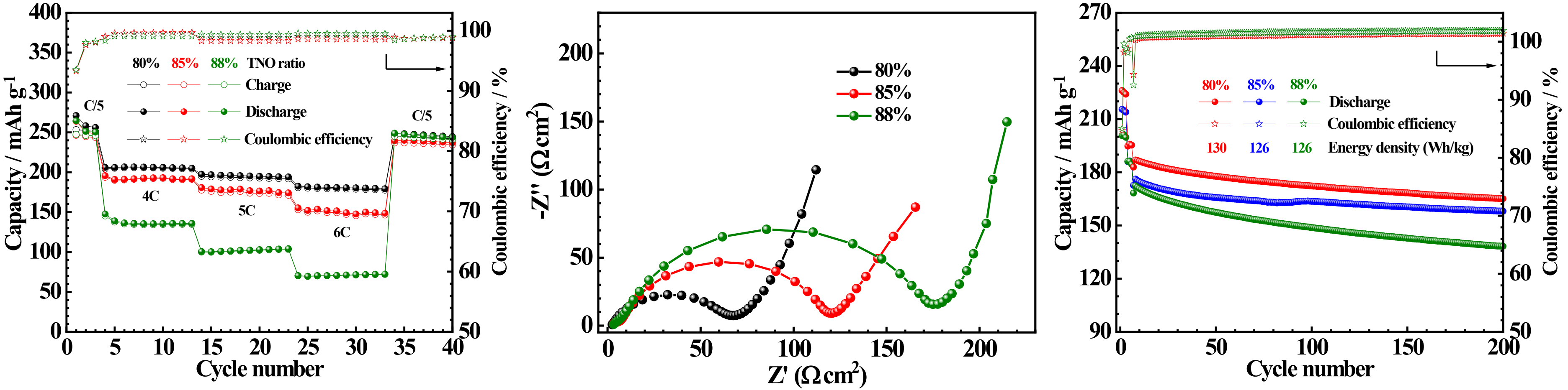
UTK Contributors: Hailong Lyu, Tao Wang

Technical Back-Up Slides

THE UNIVERSITY OF TENNESSEE KNOXVILLE
BIG ORANGE. BIG IDEAS.®

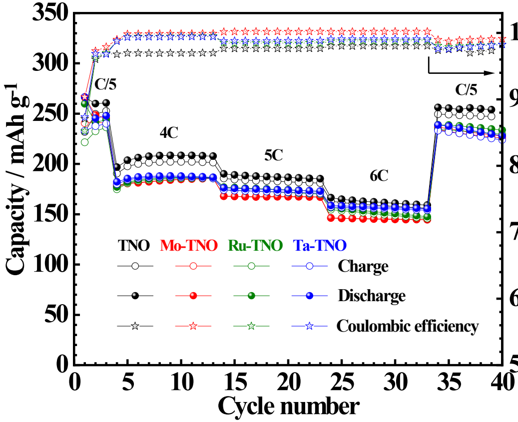
OAK RIDGE National Laboratory

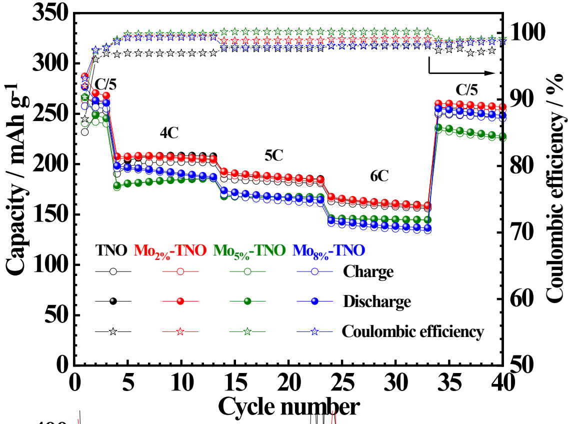
Optimization of TNO mass proportion in electrode fabrication

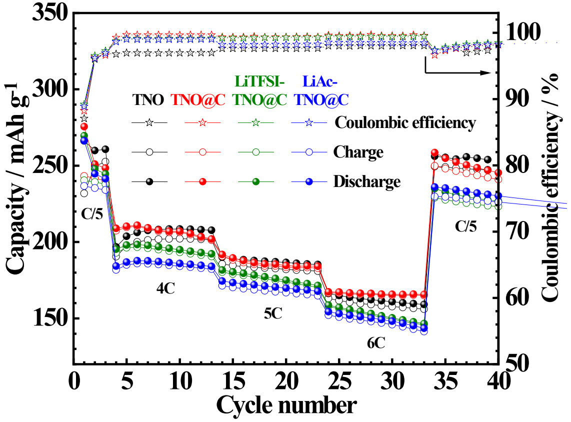


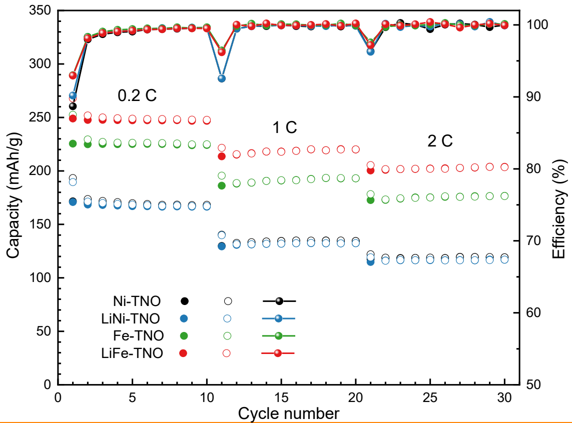
- Specific capacities of the b-TNO half-cells decrease with the increasing weight percentage of TNO at high current rates, mainly due to the lower electronic conductivity with decreased amount of conductive carbon (i.e. high cell impedance).
- The b-TNO electrode with 80% TNO mass loading delivers the best cycling performance and therefore was selected for further optimization, as it seems unworthy of losing about 20% capacity with only 5 wt.% gain of TNO loading.

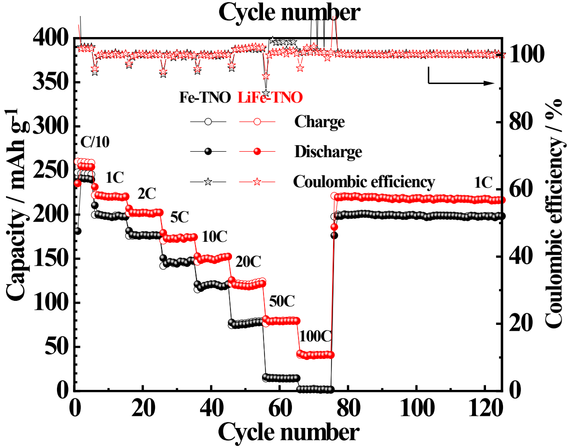
Different doping strategies





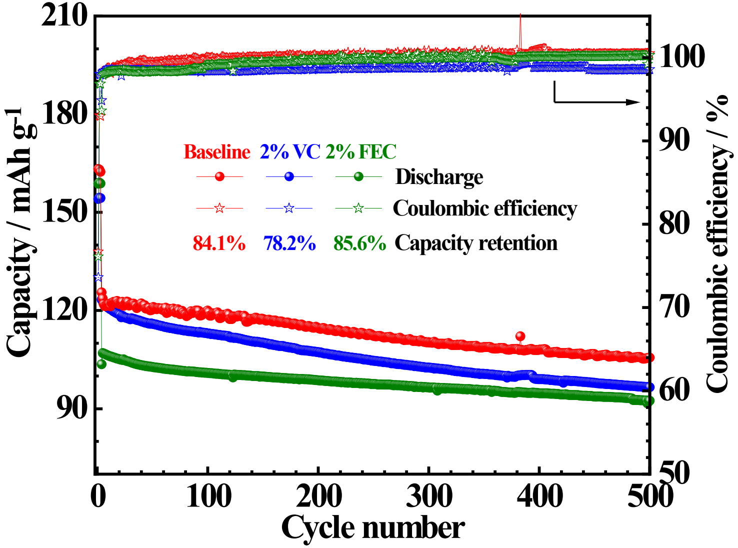


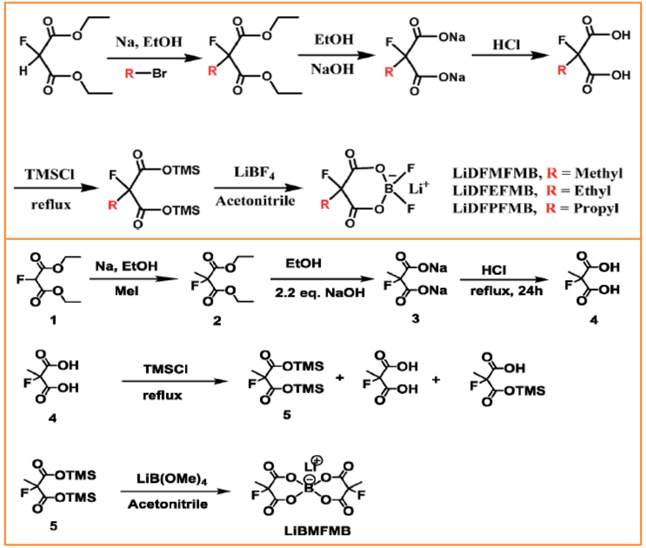




- Various transition metals and different doping strategies have been tried; however, no better performance than pristine TNO has been achieved.

Evaluation of electrolyte additives

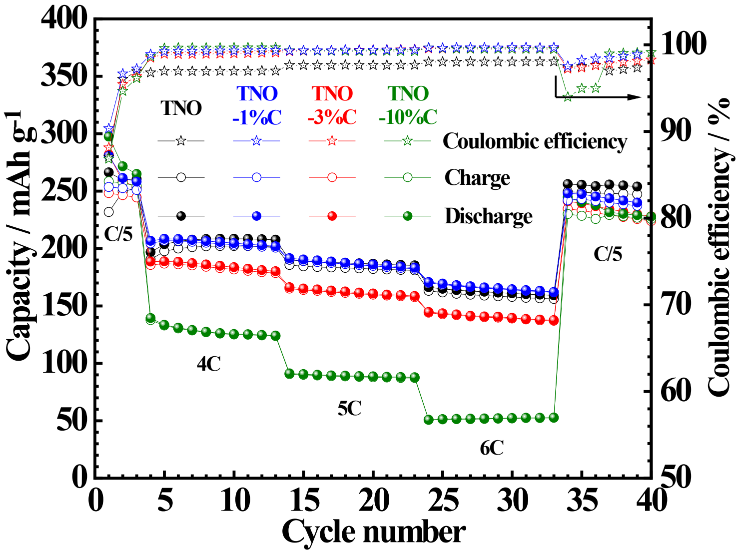


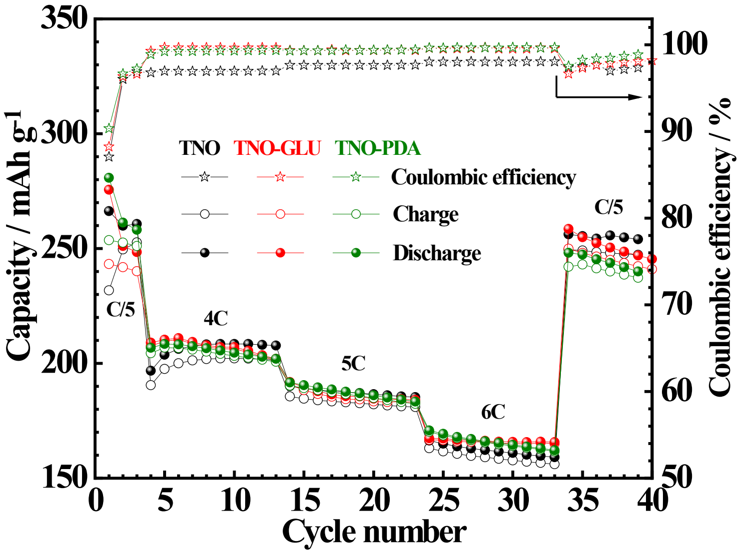


- ➢ Both commercial additives VC and FEC cannot improve the XFC performance of the NMC/TNO full-cells.
- ➢ The two types of new lithium malonatoborate salts, LiBMFMB and LiDFMFMB, have been synthesized according to previous reports. The evaluation of them as electrolyte additives for NMC/TNO full-cells is ongoing.

1. Wan, S., et al., *Chem. Commun.* **2015,** *51* (48), 9817-9820.
2. Sun, X. G., et al., *J. Mater. Chem. A* **2017,** *5* (3), 1233-1241.

Large-scale carbon coating





- Dopamine is used as carbon source to prepare nitrogen doped TNO@C with different carbon contents, exhibiting good high rate performance with 1 wt.% carbon coating.
- Carbon coated TNO with dopamine can deliver similar properties to the one with glucose, while the former is much easier for large scale production.